GB1071910

Title:
Laminate material and process of making same

Abstract:

A laminate article comprises a paper layer coated with a film forming non-aromatic hydrocarbon olefin polymer, with or without the aid of an adhesion promoting agent, the polymer being coated with a metal layer and the metal layer coated with a film-forming non-aromatic hydrocarbon olefin polymer. The olefin polymer may be a polymer of a mono-olefinic monomer containing from 2 to 8 carbon atoms e.g. ethylene propylene or butylene. The layer of olefin polymer on the metal layer may be transparent. The metal layer may be of tin, aluminium, magnesium, lead, nickel, zinc, gold or silver, and may be less than 0.04 mil thick. An intermediate adhesion promoting layer of a polyalkyleneimine containing alkylene units having from 2 to 4 carbon atoms may be disposed between the paper and olefin polymer layer. The polyalkyleneimine may be polyethyleneimine and may be applied with a gravure roll. The laminate article is made by depositing e.g. by extrusion, a molten layer of the film forming non-aromatic hydrocarbon olefin polymer over the layer of metal and solidifying the olefin polymer on the metal layer. The layer of paper, polyolefin or metal may be subjected to a methane flame or an electrostatic discharge before depositing the olefin polymer over the layer of metal. The molten polyolefin may be passed any distance through the atmosphere from the outlet of the die to the surface to be coated. Advantageously the distance should be not more than 12 inches e.g. 6 to 10 inches. The laminate may be heat sealed and used for packaging foodstuffs, cosmetics, and medicinals.

PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Laminate Material and process of making same

We, THE DOW CHEMICAL COMPANY, a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of Midland, County of Midland, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a laminate wrapping or packing material, and particularly laminate material adapted for the wrapping of foodstuffs and other consumer products.

The present invention provides a composite laminate structure having a first or substrate layer of paper, a second layer of a film-forming non-aromatic hydrocarbon olefin polymer uniformly deposited over the paper layer, a third layer of a metal uniformly depoisted over the second layer of olefin polymer, and a fourth layer of a film-forming non-aromatic hydrocarbon olefin polymer uniformly deposited over the metal layer.

The laminate structures of the present invention are prepared by first extrusion coating the paper substrate with the olefin polymer by expelling a molten sheet or screen of the polymer on the paper web and immediately cooling and solidifying the olefin polymer layer by contacting it with a smooth shiny chill roll. This provides a smooth, uniform coating of olefin polymer susceptible to having deposited thereon a smooth lustrous metal layer or coating by passing the polymer coated paper through a suitable vacuum metallizer. After the metal layer is uniformly deposited over the polyolefin layer, a second layer of an olefin polymer is deposited over the metal layer by extrusion coating a molten layer of the olefin polymer over the metal in the same fashion as the polymer coating is applied over the paper.

The laminate structure of the invention is perspectively illustrated in Figure 1 of the accompanying drawing.

The preferred process for preparing the laminate structure in accordance with the invention is schematically illustrated in Figure 2 of the drawing.

The laminate article of this invention is advantageously employed as a package material or as an overwrap for packages because of its good strength coupled with light weight and high degree of flexibility and excellent barrier properties. Frequently, the total thickness of the composite laminate structure may be as little as 1 to 2 mils (.025—.05 mm). However, thicker structures can be made if desired. Moreover, packages formed or covered with the laminate material are readily heat sealed, thus eliminating the use of an adhesive. Because of the relative thinness of the present structure the heat seal is quickly and efficiently formed even though the heating surfaces or platens may be applied to the paper side of the laminate structure. The polyolefin coating over the metal deposit thus serves to protect the metal against abrasion or chemical attack or the like and simultaneously provides a heat sealable layer. Additionally, the present laminate structure has an appealing, highly lustrous and reflective appearance when a transparent layer of polyolefin is applied over the metal.

The laminate material can be used as an ovewrap, as indicated, or it can be employed in the formation of the package itself. Generally, it is so arranged that the paper layer is exposed on the exterior of the package since it is readily made highly decorative by printing and is well suited for printing thereon direc-

tions and advertising. When a liquid is packaged in a package formed of the laminate material the polyolefin layer ideally forms the inner layer, although the paper layer could be used as the inner layer if a high wet-strength paper, such as resin impregnated paper is employed.

Any type of paper and paper thickness can be employed as the substrate layer, although in keeping with the precepts of the invention a relatively thin and flexible paper layer is advantageously utilized. Any of the treated, filled, sized or resin-impregnated papers can be employed; however, generally to be avoided are materials in or on the paper surface that tend to interfere with the adhesion of the polyolefin layer to the paper substrate.

The non-aromatic hydrocarbon olefin polymer that is extrusion coated over the paper substrate and over the metal coating or deposit according to the present invention are generally prepared by polymerization of olefin and preferably mono-olefinic aliphatic olefin monomers such as ethylene (including polymerization to low density and high density or linear polyethylene), propylene, butylene and so forth (including polymerizable mixtures thereof) that contain from 2 to 8 carbon atoms, which monomeric olefins are frequently known as 1-olefins due to their characteristic terminally unsaturated structure.

The polyolefin can be applied to the paper substrate or surface of the metal deposit, whichever is applicable, from an extruder of any conventional or desired construction, adapted to expel a falling sheet-like layer or curtain of molten polyolefin through a suitable die orifice onto the paper or metal surface. It is generally advantageous to maintain the polyolefin in the extruder, particularly when it is polyethylene, at a temperature sufficiently high to ensure its remaining in a fused and molten condition after being passed from the die to fall through the air as a layer on the surface to be coated. Thus, it is generally desirable for the extruded polymer, when it is polyethylene for example, to be at a temperature of 175—190°C. at actual contact or juncture with the surface. This generally requires the molten polymer in the extruder barrel, as it leaves the die lips, to be at a temperature between 285—315°C.

Although the molten polyolefin may be passed any distance through the atmosphere from the outlet of the die to the point of juncture with the surface to be coated, it is generally advantageous for the distance to be not more than 12 (30.5 cm) advantageously about 6 to 10 (15.25 to 25.4 cm) inches to be utilized.

Immediately upon being applied, the polyolefin layer is chilled, solidified and laminated in place by, for example, the action of a shiny chill roll which is maintained at a temperature above the sticking temperature of the polyolefin but below its fusion point, which temperature is most advantageously maintained in the range from 25 to 40°C.

After being laminated to the paper substrate, the composite product may be taken up by any suitable means or in any desired manner, such as onto a take-up roll and stored prior to being coated on the polyolefin surface with the metal deposit in a vacuum chamber.

Any desirable thickness of the polyolefin can be applied over the paper substrate and metal deposit. With the paper, it is important that a thick enough layer be used to assure a relatively smooth surface and fill the imperfections of the paper surface so that out-gassing of the paper and the objectional results thereof are prevented. The ultimate use designed for the laminate product will also influence the thickness of the polyolefin layer. Advantageously, a polyolefin layer is applied having a thickness between 0.25 mil and 10 mils (.0064 to .254 mm) and frequently the beneficial thickness will run from 0.5 to 2 mils (.0127 to .05 mm).

The deposit of the metal coating over the polyolefin layer may be obtained by known thermal evaporation or cathodic sputtering methods.

Any metal capable of being vacuum metallized as described can be utilized in the practice of the present invention including aluminum, magnesium, tin, lead, nickel, zinc, gold or silver. Preferably, tin is employed, especially when the laminate material is used to package food, cosmetics, medicinals and the like products because of the lack of odor.

Actually, only a very thin film of metal need be deposited on the surface of the polyolefin surface. Generally, the thickness of the metal deposit does not exceed a layer on the order of about 0.00004 inch (0.04 mil or about 0.001 millimeter) and generally is in the neighbourhood of 2 to 3×10^{-6} inch (5.08 to 7.62×10^{-5} mm) thick. Thicknesses are conveniently measured by electro conductivity methods.

After being provided with the coating of metal, the composite structure of paper/polyolefin/metal is then processed through a second polyolefin extrusion to apply over the metal deposit a layer of polyolefin, which may be the same or a different polyolefin than that applied over the paper, according to the procedure described above.

If desirable or necessary, either the paper or polyolefin layer applied thereover or metal layer may be provided with beneficial adhesion promoting agents or other treatments such as oxidizing treatments by exposing the surface to a methane flame or to an electrostatic treatment in order to effect a tighter and more durable bond between the respective layers of the present composite laminate structure. In an embodiment an intermediate adhesion promoting layer of a polyalkyleneimine containing

alkylene units having from 2 to 4 carbon atoms is disposed between the paper and the olefin polymer layer.

In order to illustrate further the present invention Examples of several different laminate structures were prepared and tested. The laminate structures are prepared by first treating one of the surfaces of a paper substrate with a solution of polyethyleneimine. About 1.5 weight percent solution of the polyethyleneimine in ethanol is applied to one of the surfaces of a paper substrate with a gravure roll, after which the substrate is dried at about 65°C. in an oven leaving a deposit of about 15 grams of polyethyleneimine per 1000 square feet (92.9 sq. m.) paper surface.

The treated paper is taken up on a stock roll and then positioned on the delivery roll of an extruder. The treated roll is delivered to the nip rolls of an extruder at a linear rate of about 100 feet (30.48 meters) per minute. The paper is passed between the rolls, consisting of back up roll and a shiny chill roll (about 25°C.), and about a 0.5—1 mil (.0127—.0254 mm) layer of polyethylene is applied to the polyethyleneimine treated surface by feeding a molten polymer layer in the form of a falling sheet or curtain (through about an 8-inch (20 cm) fall) from the die lip to the nip of the rolls. The temperature of the polyethylene in the barrel of the extruder is about 315°C. Its temperature at contact with the paper substrate is about 190°C. The polymer is cooled and solidified by the chill roll, and the coated paper is wound on a storage roll. Some of the polyethylene surfaces are then passed over in apposition to an electrostatic discharge to treat the surface in order to effectuate better adherence of the tin coating.

The roll of polyethylene coated paper is then placed in a vacuum metallizer and threaded up such that the web or rolled sheet is unwound from the delivery roll, passes under a chill roll positioned above the crucibles, the polyethylene surfaces facing the crucibles, and taken up on a take-up roll. A quantity of tin is placed in several crucibles under and aligned along the length of the chill roll so that the full width of the surface will receive a deposit of tin. A vacuum of about 10 microns mercury is effected in the metallizer and the crucibles are heated to about 1300°C. The web is thus coated with a thin tin deposit at a rate of 80—175 feet (24—53 meters) per minute. An excellent, lustrous, uniform layer of tin about 0.000002 inch (5.08×10^{-5} mm) thick on the polyethylene surface is produced and there is no evidence of pin-holding nor of any offensive odor.

Subsequently, the tin surface is provided with a polyethylene coating in the manner described above for applying the polyethylene coating to the paper substrate. The resulting laminate structures have good appearance, are odor free, light weight, flexible, possess highly acceptable barrier properties and are readily heat sealable to good seal strengths. The results of various tests performed on the laminate structures are set forth in the following table.

Laminate Structure Paper/Polyethylene(PE)/Tin/Polyethylene(PE) (Wt./ream) (Wt./ream) (Wt./ream)	(3)Heat Seal Strength lb.	kg.	Moisture Vapor Transfer Rate (grams moisture/ 24 hrs./100 in.^{2} [645 sq. cm.])	Gas Transfer Rate (cc. gas/24 hr./100 in.^{2} [645 sq. cm.])
13.6 kg Kraft/3.18 kg PE(1)/tin/4.53 kg PE	3.15	(1.43)	—	4.68
13.6 kg Kraft/3.18 kg PE(2)/tin/9.98 kg PE	4.11	(1.86)	—	3.00
11.3 kg Sulfite/3.18 kg PE(1)/tin/9.98 kg PE	4.74	(2.15)	—	12.0
11.3 kg Sulfite/3.18 kg PE(2)/tin/9.98 kg PE	4.36	(1.98)	—	5.8
11.3 kg pouch/3.18 kg PE(1)/tin/9.98 kg PE	4.10	(1.86)	0.012(4) 0.024(5)	3.98

(1) PE surface electrostatically treated

(2) PE surface not electrostatically treated

(3) Heat seal made at 150° C., 30 spig, at 1 second dwell, seal formed between polyethylene surfaces pressed together, heat applied from paper side of laminate structure, measured on Instron (Registered Trade Mark) tester

(4) Flat

(5) Creased

Packages made from the laminate materials by heat sealing are separately filled with a liquid shampoo, a hair cream dye solvent, a sour cream mix, calcium chloride, water and a concentrated liquid chlorine bleach. All of these materials are satisfactorily contained in these packages at room temperature.

WHAT WE CLAIM IS:—

1. Laminate article having a paper layer coated with a film-forming non-aromatic hydrocarbon olefin polymer, with or without the aid of an adhesion promoting agent, the polymer is coated with a metal layer and the metal is coated with a film-forming non-aromatic hydrocarbon olefin polymer.

2. Article of Claim 1, wherein the olefin polymer is a polymer of a mono-olefinic monomer containing from 2 to 8 carbon atoms.

3. Article of Claim 2, wherein the olefin polymer is polyethylene.

4. Article of any one of Claims 1 to 3, wherein the metal layer is less than 0.041 mil (.001 mm) thick.

5. Article of any one of Claims 1 to 3 wherein the metal layer is tin.

6. Article of Claim 1 wherein an intermediate adhesion promoting layer of a polyalkaleneimine containing alkylene units having from 2 to 4 carbon atoms is disposed between the paper and olefin polymer layer.

7. Article of Claim 6 wherein the polyalkyleneimine is polyethyleneimine.

8. Process for making a laminate article which comprises (a) depositing a molten layer of a film-forming, non-aromatic hydrocarbon olefin polymer over a paper substrate and solidifying the olefin polymer on the paper, (b) depositing a uniform layer of a metal over the olefin polymer layer by vapor deposition, and (c) depositing a molten layer of a film forming, non-aromatic hydrocarbon olefin polymer over the layer of metal and solidifying the olefin polymer on the metal layer.

9. Process of Claim 8, wherein the olefin polymer is a polymer of a mono-olefinic monomer containing from 2 to 8 carbon atoms.

10. Process of Claim 9, wherein the olefin polymer is polyethylene.

11. Process of any one of Claims 8 to 10 wherein the deposited layer of metal is less than 0.04 mil (.001 mm) thick.

12. Process of any one of Claims 8 to 10, wherein the metal layer is tin.

13. Process of Claim 8 wherein a polyalkyleneimine containing alkylene units having from 2 to 4 carbon atoms is applied to the surface of the paper substrate over which the olefin polymer is to be applied.

14. Process of Claim 13, wherein the polyalkylemeimine is polyethyleneimine.

15. Process of any one of Claims 8 to 10 wherein the layer of metal is subjected to an electrostatic discharge before depositing the olefin polymer over the layer of metal.

16. Process for preparing laminate articles substantially as hereinbefore described with reference to the specific Examples.

17. Laminate articles whenever prepared by the process of any one of Claims 8 to 16.

18. Laminate article substantially as described and illustrated in Figure 1 of the accompanying drawing.

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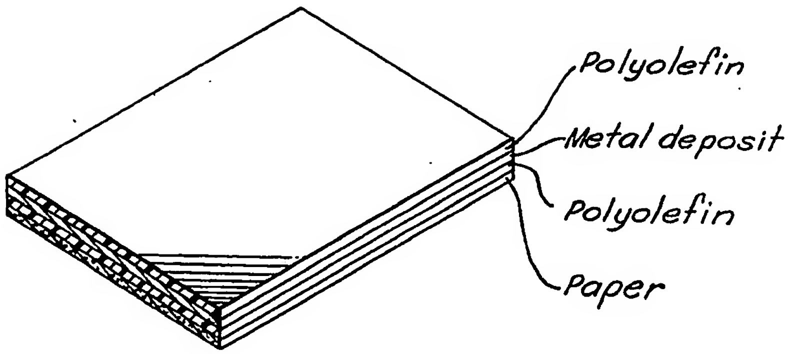
Polyolefin
Metal deposit
Polyolefin
Paper

Fig. 1

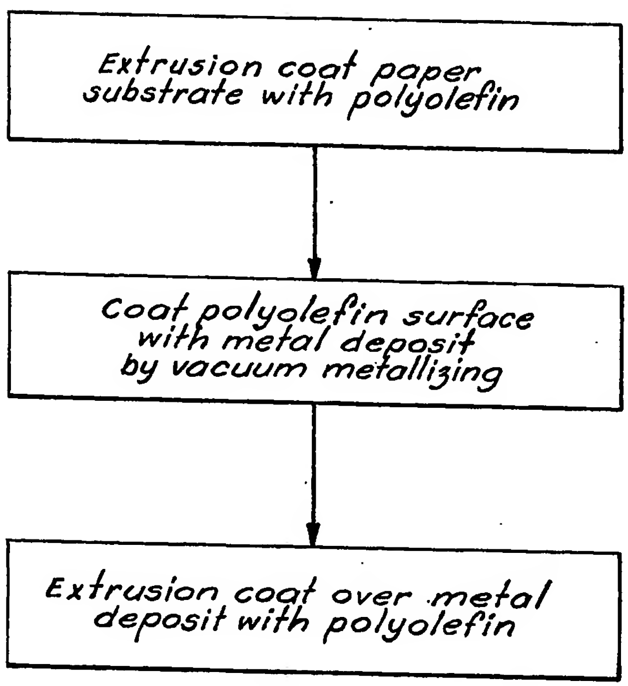
Extrusion coat paper substrate with polyolefin
Coat polyolefin surface with metal deposit by vacuum metallizing
Extrusion coat over metal deposit with polyolefin

Fig. 2